AgI-MOR Loading Effect on the Durability of the Sandia Low Temperature Sintering GCM Waste Form

Fuel Cycle Research & Development

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SUMMARY

Herein, we study the durability of the Sandia Bi-Si oxide Glass Composite Material (GCM) waste form when formulated with different weight percent levels of AgI-MOR. The post-iodine exposure AgI-MOR material was provided to SNL by ORNL. Durability results for the GCM fabricated with 22 and 25% AgI-MOR indicate releases of Ag and I at the same low rates as 15% AgI-MOR GCM, and by the same mechanism. Iodine and Ag release is controlled by the low solubility of an amorphous, hydrated silver iodide, not by the surface-controlled dissolution of I$_2$-loaded Ag-Mordenite. Based on this data, we postulate that much higher loading levels of AgI-MOR are probable in this GCM waste form, and limits will govern by retention of mechanical integrity of the GCM versus the solubility of silver iodide.

ACKNOWLEDGEMENTS

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ABBREVIATIONS AND ACRONYMS

AgI	Silver Iodine
Al	Aluminum
ASTM	American Society for Testing and Materials
Bi	Bismuth
°C	Degrees Celsius
CH_3I	Methyl iodide
cm	Centimeter
d	diameter
FCRD	Fuel Cycle Research and Development
GCM	Glass Composite Materials (waste form)
I_2	Iodine (gas)
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
µ	Micro
M	mole/liter
MOR	Mordenite Zeolite
O	Oxygen
ORNL	Oak Ridge National Laboratory
s	Second (time)
Si	Silicon
SNL	Sandia National Laboratories
SPFT	Single Pass Flow Through test
XRD	X-ray Diffraction
Zn	Zinc

1.   INTRODUCTION

As part of our ongoing research effort to understand the durability and materials processability of the low temperature sintering Sandia Waste Form for iodine capture materials, we have undertaken a study in which the effect of weight percent loading of I_2-loaded Ag-Mordenite on the durability of the final Bi-Si Glass – Glass Composite Material (GCM) is determined.

The chemical and physical controls over iodine release from candidate [129]I waste forms must be quantified to predict long-term waste form effectiveness.   Ag-Mordenite will likely be an important waste form component because of its ability to remove [129]I from waste streams and convert it to AgI and/or sorb it (e.g. Chapman et al., 2010). Silver iodide is relatively insoluble in water, $K_{sp} = 10^{-16.1}$ at 20°C, so Ag-Mordenite should retain [129]I for long periods of time. Encapsulating [129]I-loaded Ag–Mordenite (AgI–MOR) into a durable solid waste form should limit potential releases of [129]I further. Low temperature sintering Glass Composite Materials (GCMs) are candidates for encapsulating AgI-MOR. GCMs contain both crystalline and glass phases, and are easier to synthesize, less expensive, and can achieve higher waste loadings than traditional ceramic waste forms (e.g. Garino et al., 2011).

Herein we study the durability of the Sandia low temperature sintering Bi-Si oxide Glass Composite Material (GCM) waste form when formulated with the increased weight loadings of 22 and 25% Ag-MOR; material provided to SNL by ORNL. We use a Single Pass Flow Through (SPFT) test to determine if the AgI-MOR content and overall GCM AgI-MOR composition affects the rate at which iodine and silver are released from the waste form, and therefore its durability. These results complement our previous efforts to document iodine loading, pH, temperature, and particle size impacts on the durability of the GCM AgI-MOR waste form (Nenoff et al., 2012, 2013a, 2013b, 2014).

2.   EXPERIMENTAL METHODS

AgI-Mordenite and GCM Preparation

Two I_2 loaded AgI-MOR GCM samples were made from AgI-MOR samples provided by ORNL. Specifically, 22 and 25 wt% of ORNL AgI-MOR that had been 8.7% I_2 loaded were

combined with 78 and 75 wt%, respectively, of Ferro EG2922 glass powder, a commercially available Bi–Si-oxide glass (3 μm average particle size, a density of 5.8 g/ cm^3, coefficient of thermal expansion of 7.8 x 10^{-6} / °C, from Ferro Corp., Cleveland, OH). The glass has a composition of: 7.8 wt% ZnO, 63.4 wt% Bi$_2$O$_3$, 5.4 wt% Al$_2$O$_3$, 23.4 wt% SiO$_2$. An amount of Aldrich silver flake equal to 5.5 % of mass of the AgI-MOR was added to react with the I$_2$ vapor that desorbs from the AgI-MOR during heating.

After sintering, the samples were hand ground with an alumina mortar and pestle to < 38 μm before spex milling (8000M, Spex Sample$^®$Prep$^®$, Metuchen, NJ) for 10 minutes using an silicon nitride mill and ball. The surface area was measured using the BET method. The ground materials had BET surface areas of 3.4287 m^2/g (ORNL AgIMOR 22% EG2922 78%), and 6.4239 m^2/g (ORNL AgIMOR 25% EG2922 75%).

Characterization:

The materials were examined using powder X-ray diffraction (XRD, Siemens Kristalloflex D 500 diffractometer, Bruker-AXS Inc., Madison, WI), before and after heating in the TGA/DSC. Samples of the AgI-MOR GCMs with varying particle sizes of AgI-MOR were examined using scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM, FEI NovaNano SEM 230 and EDS, EDAX Genesis Apex 2 with an Apollo SDD detector). Optical microscopy was performed on an AM4013TL Dino-Lite Premier digital microscope.

Inductive Coupled Plasma - Mass Spectrometry (ICP-MS):

Aqueous samples were first filtered of any particulates using a 0.2 μm polypropylene filter media. Those solutions were then analyzed for elemental content using a Perkin Elmer (Groton, CT) Elan 6100 DRC ICP-MS instrument. Liquids were aspirated directly into the instrument without modification and the instrument was operated in the semi-quantitative mode. This mode compares signal from a multi-element standard analyzed the same day with known relative instrument response factors to calculate concentration of those elements detected in the sample. Two multi-element standards (CLMS-1 and CLMS-2, Spex Certiprep, Metuchen, NJ), covering 46 elements, were used for these tests.

Samples were tested for pH immediately following ICP-MS analysis using an Orion (Thermo Fisher Scientific, Waltham, MA) model 720A pH meter. The pH probe was calibrated using a 3-point calibration at 25°C (pH: 4.00, 7.00 and 10.00) using buffered pH standards (Thermo Fisher Scientific, Waltham, MA). Each water sample was measured in triplicate. The pH probe was rinsed with DI water after every reading, and the excess rinse water gently blotted off the probe to prevent any carryover to the sample tubes. After every 6 individual readings the pH probe was rechecked with a pH = 7.0 calibration solution to verify that drift was not occurring.

Single-Pass Flow-Through Test

The Single Pass Flow Through Test Method (ASTM C-1662) is traditionally used to measure nuclear waste glass dissolution rates in aqueous solutions at T < 100°C. Waste form component release rates are measured by exposing a high surface area waste form sample in a reactor to a continual flow of solution and measuring waste form component concentrations in the effluent (e.g. Chou and Wollast, 1985). 4 reactors were constructed of Tygon tubing and pipette tips containing 0.2 g of each AgI-MOR waste form. The input solution, 0.01M NaCl was pumped through the reactor beds at a rate of 0.18 L/day. Dissolution measurements were made at 25°C. Effluents were analyzed for pH, and for Ag, I, Zn, and Si, effluent levels in ppb, by ICP-MS in semi-quantitative mode (Table 1). Samples were tested for pH immediately following ICP-MS analysis using an Orion (Thermo Fisher Scientific, Waltham, MA) model 720A pH meter. The pH probe was calibrated using a 3-point calibration at 25°C (pH: 4.00, 7.00 and 10.00) using buffered pH standards (Thermo Fisher Scientific, Waltham, MA). Each water sample was measured in triplicate. The pH probe was rinsed with DI water after every reading, and the excess rinse water gently blotted off the probe to prevent any carryover to the sample tubes. After every 6 individual readings the pH probe was rechecked with a pH = 7.0 calibration solution to verify that drift was not occurring. Tabulated pHs represent the average of 3 measurements.

Table 1. SPFT effluent levels (ppb) and AgI concentration product.

Sample	Hours	pH	Si	Ag	I	Zn	log[Ag][I]
ORNL AgIMOR 22% EG2922 78%							
1	50	5.82	254	30.0	8.3	372	-13.74
2	54	5.40	259	29.0	16.7	365	-13.46
3	76	5.42	259	24.4	20.1	292	-13.45
4	97	5.88	287	20.2	16.6	291	-13.62
5	99	5.18	291	19.9	15.7	312	-13.65
6	100	5.81	294	18.4	15.5	300	-13.69
7	123	5.28	294	19.5	14.7	277	-13.68
ORNL AgIMOR 25% EG2922 75%							
1	24	5.60	232	30.0	9.4	274	-13.69
2	48	5.61	217	27.6	18.9	299	-13.42
3	72	4.95	258	25.1	20.1	257	-13.44
4	96	5.13	234	22.3	15.8	217	-13.59
5	98	4.93	244	23.4	14.9	231	-13.60
6	100	5.05	256	22.7	13.5	239	-13.65
7	124	4.80	284	22.2	13.3	224	-13.67

3.   RESULTS

The samples studied included two different weight percent loadings of AgI-MOR encapsulated in the Bi-Si Glass to form GCM waste forms: 22 wt % and 25 wt%. These sizes were chosen because they are above traditional weight percent loadings and the resultant waste form maintains its physical integrity after sintering. By selecting a range of weight loadings of AgI-MOR with the same iodine weight loading (8.7 wt %), a range of processing conditions can be obtained for future uses in production of the waste form. Samples were studied by XRD, optical microscopy and SEM-EDS. All materials characterization is presented in Appendix A.

Steady-state effluent pHs were ~ 5.0 – 5.2 for each run.   Ag effluent levels reached steady-state values within ~ 4 days and are essentially the same for each waste form, in the range of 20 - 22 ppb (Figure 1). Steady state iodine effluent levels were ~ 13-14 ppb and reached constant, steady-state values after ~ 4 days of reaction (Figure 1). Steady state log[Ag][I] values are ~ -13.7. For comparison, previous durability measurements of 15% I_2-loaded AgI-MOR GCMs under similar conditions produced Ag and I effluent levels of ~25 - 46 and 3-12 ppb (Nenoff et al., 2013c), and steady-state log[Ag][I] values of -13.4 – -14.2. Because of the similarity in results, there appears to be little effect of AgI-MOR content, at least from 15 – 25% AgI-MOR,

on effluent silver and iodine release from the GCM waste form. The relative constancy of Ag
and I levels supports the hypothesis that AgI solubility controls Ag and I release. Note that the
log product of the measured Ag and I levels cluster around a constant value of $10^{-13.7}$, which is
higher than the theoretical AgI solubility product of $10^{-16.1}$. Ag and I are most likely being
released from a more soluble, amorphous and possibly hydrated, AgI phase in the dissolving
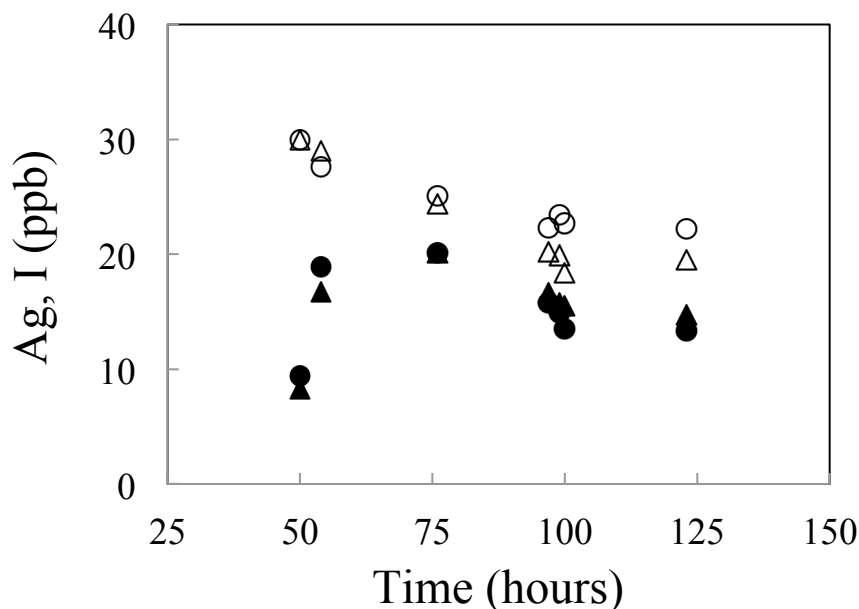waste form.

Figure 1. Ag (unfilled symbols) and I (filled symbols) effluent levels as a function of time.
Circles = 22% AgI-MOR; squares = 25% AgI-MOR.

4.   CONCLUSIONS AND FUTURE WORK PLANS

As part of our ongoing research effort to understand the durability and material processability
of the low temperature sintering Sandia Waste Form for iodine capture materials, we have
undertaken a study of the effect of AgI-MOR loading on the durability of the final Bi-Si Glass –
Glass Composite Material (GCM).

AgI-MOR weight loading level in a GCM waste form appears to have little effect on iodine
or silver release because, as expected, both are limited by the low solubility of AgI. The higher
effluent portion of Ag relative to I (Figure 1) suggests that Ag leaching from the waste form

controls equilibrium levels of iodine. Higher Ag leach rates will lower I levels issuing from a degrading waste form.

Our results suggest that relatively high loadings of AgI-MOR (25%) will not result in higher I release from AgI-MOR waste forms. The formation of amorphous AgI appears to limit overall I release independent of glass waste form material.   Based on this data, we postulate that much higher loading levels of AgI-MOR are probable in this GCM waste form, and limits will be governed by the retention of GCM mechanical integrity versus the solubility of silver iodide.

On-going research will focus on further optimizing the GCM composition especially due the results of earlier studies that showed inert sintering atmosphere enabled the removal of Ag flake addition from the GCM starting materials. Morphology changes due to increased loading levels in the AgI-MOR GCM and effects on durability will also be addressed. For example: the XRD patterns from this present study indicate very minor measureable amounts of Eulytite formation in the GCM while different weigh percent loadings < 150 μm particle size resulted in much larger concentrations of Eulytite in the final GCM. We will continue to study iodine loaded Ag-MOR from complex streams (eg., H_2O, I_2, CH_3-I, NO_x, etc.) and how this capture material will interact with the glass in GCM formation and resulting durability. Furthermore, we will focus on the scaleability of the GCM using the baseline composition developed over the past few years.

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APPENDIX A: Materials Characterization
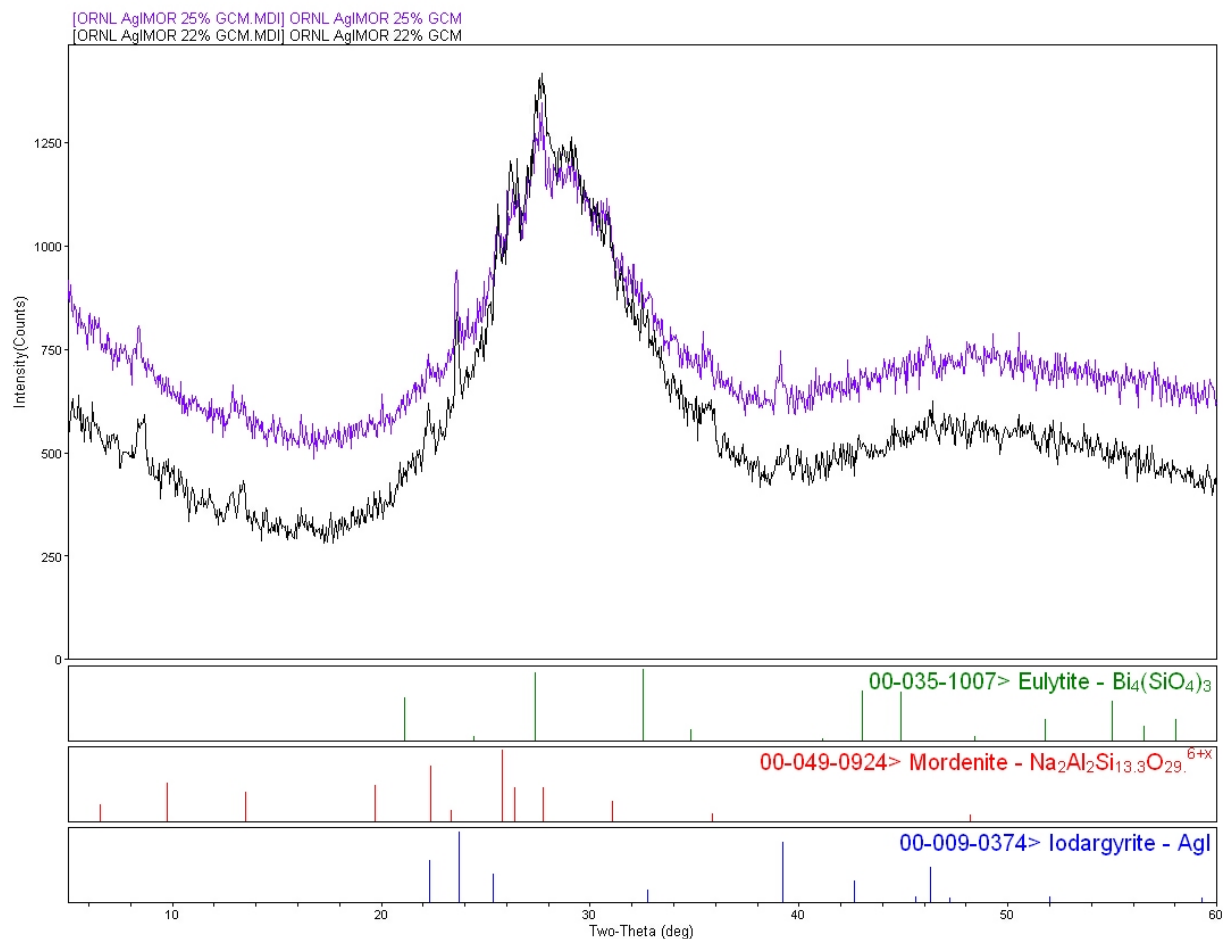
Powder X-ray Diffraction Data

Figure A1: XRD of GCMs loaded with AgI-MOR (8.7 wt% Iodine loading) from ORNL. The bottom pattern is for 22 wt % AgI-MOR loaded in the GCM; the top pattern is for 25 wt % AgI-MOR loaded in the GCM. Minor concentrations of AgI and Eulytite are evident in the broad amorphous background pattern of the GCM glass.

Scanning Electron Microscopy Data, with EDS Elemental Analysis

Examination of this data indicates similar morphology of the GCM, independent of the weight loadings.
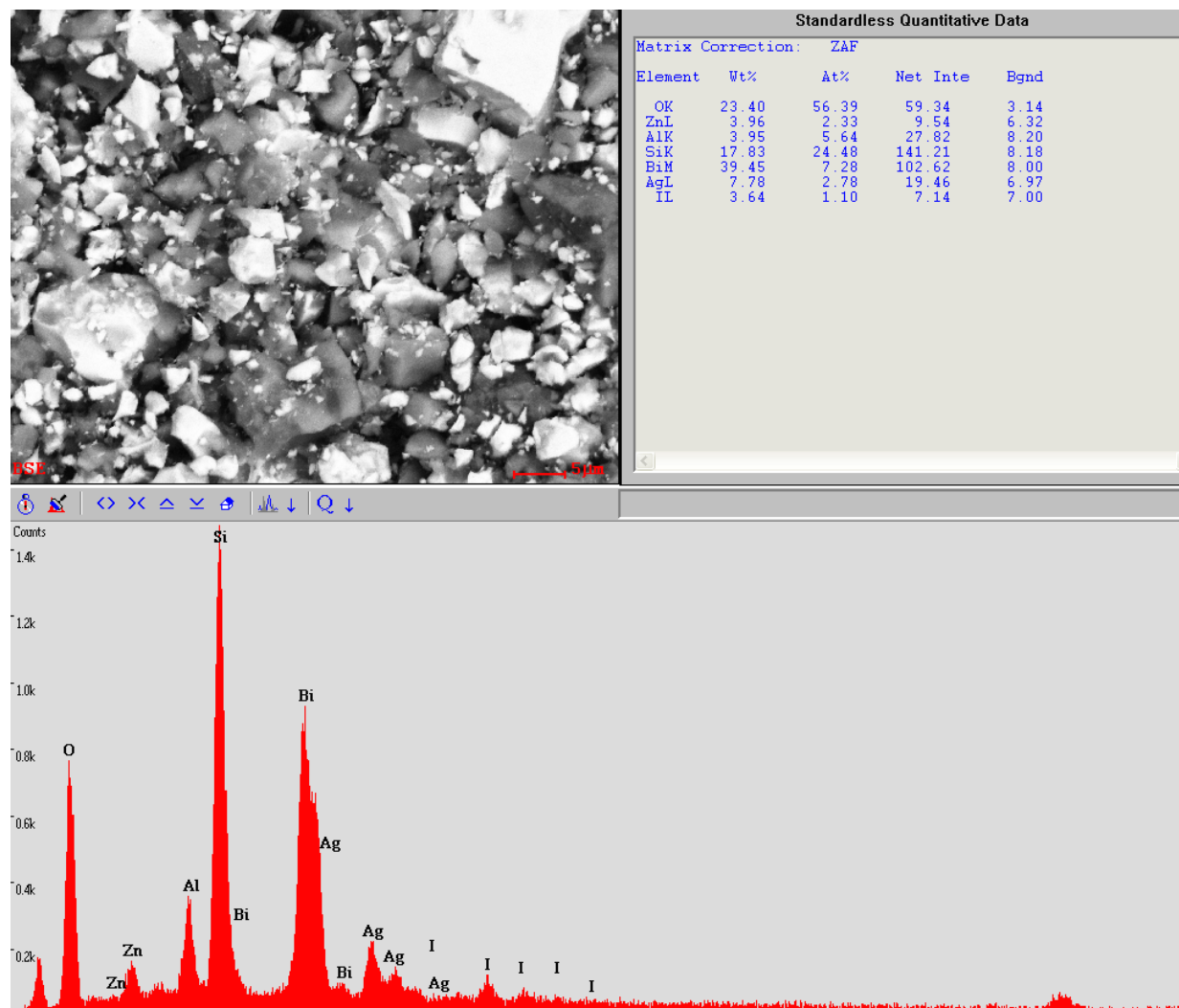

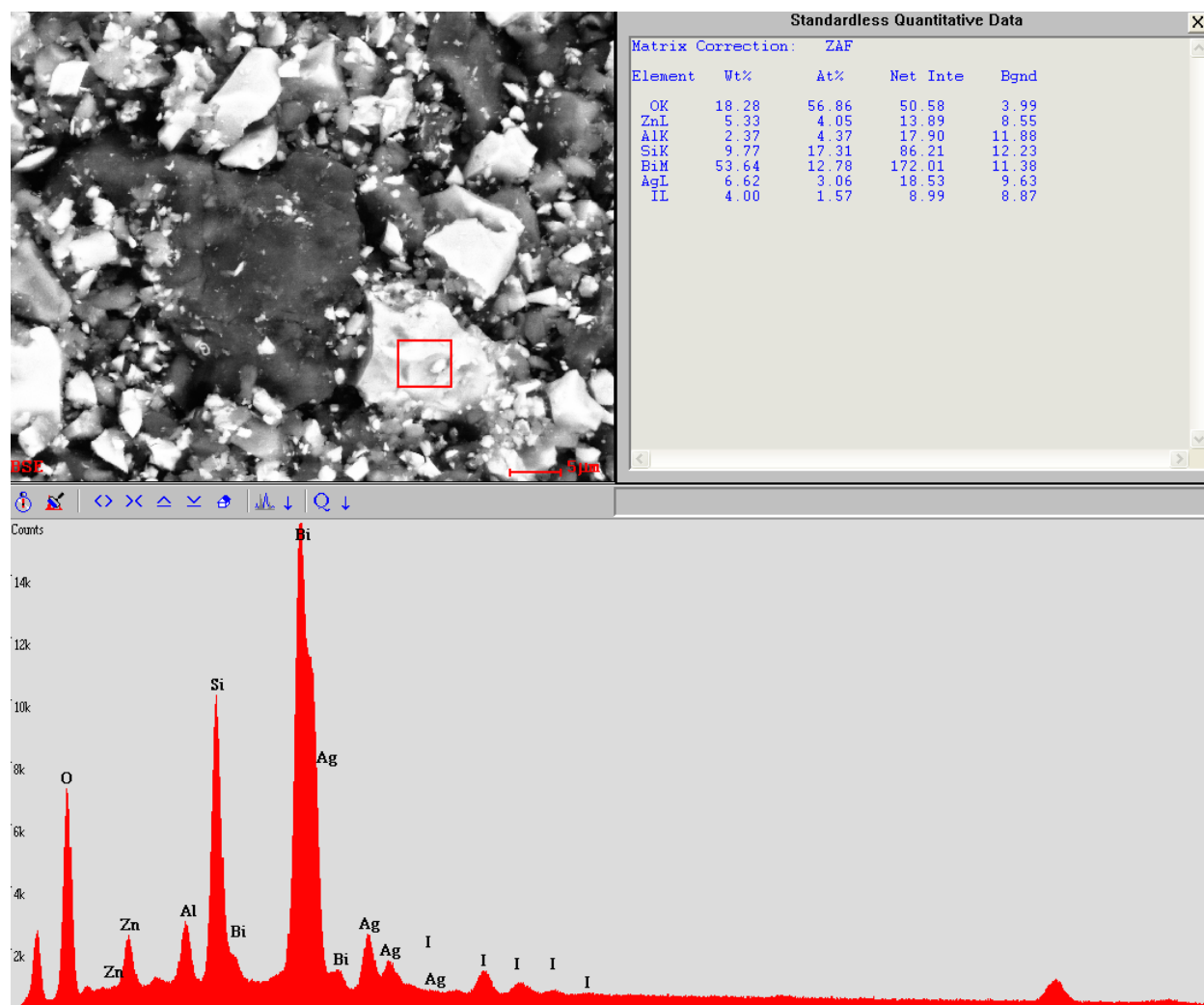Figure A2 (a): SEM/EDS of GCM fabricated with 22 wt% ORNL AgI-MOR.

Figure A2 (b): SEM/EDS of GCM fabricated with 25 wt% ORNL AgI-MOR. Focused/point EDS indicates that majority of AgI is located in the brightly colored silicon rich crystallites.

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